

Electric-pulse-induced reversible resistance change effect in magnetoresistive films

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A large electric-pulse-induced reversible resistance change active at room temperature and under zero magnetic field has been discovered in colossal magnetoresistive (CMR) $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin films. Electric field-direction-dependent resistance changes of more than 1700% were observed under applied pulses of ~ 100 ns duration and as low as ± 5 V magnitude. The resistance changes were cumulative with pulse number, were reversible and nonvolatile. This electrically induced effect, observed in CMR materials at room temperature has both the benefit of a discovery in materials properties and the promise of applications for thin film manganites in the electronics arena including high-density nonvolatile memory. © 2000 American Institute of Physics. [S0003-6951(00)00419-8]

The phenomenon of colossal magnetoresistance (CMR) has been extensively studied for the manganese perovskites based on the ReBMnO_3 (Re=rare-earth ions, B=alkaline ions) structure.^{1,2} Apart from understanding the basic mechanism underlying CMR effect, much effort has been concentrated on obtaining a large room-temperature resistance change using relatively small external stimulation.²⁻⁴ We report here a series of studies of CMR thin film materials under pulsed electric field stimulation at room temperature and with no applied magnetic field.

Among the various CMR manganites, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is unique in that it exhibits insulating behavior over the whole composition (x) range due to its narrow bandwidth of e_g electrons.⁵ The ground state of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x = 0.3-0.5$ is a charge-ordered antiferromagnetic insulator at low temperature,⁶ which can be easily driven to a metallic ferromagnetic state at low temperature by applying a large magnetic or electric field. At room temperature, however, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (with $x = 0.3-0.5$) is in the insulating paramagnetic state,⁶ and no changes in resistivity are observed even under magnetic fields of up to 8 T or applied voltage of up to 1000 V on bulk samples.^{7,8} However, under electric field pulsing of thin $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films we have observed a new electric-pulse-induced resistance (EPIR) change effect in the CMR oxide at room temperature and under no applied magnetic field.

Atomically ordered $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO) films, grown partially on a conducting layer (bottom electrode) of either $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) or Pt, or on an insulating LaAlO_3 (LAO) substrate were used as the test samples. The films were grown by conventional pulsed laser deposition on LAO substrates. The YBCO layer was also used as an atomic template for PCMO epitaxial growth, as has been effective in the atomically ordered growths of other advanced oxide thin films.^{9,10} The Pt layer was used as a control test bottom electrode. Typical thickness of the PCMO films was ~ 600 nm.

X-ray diffraction $\theta-2\theta$ scans and pole-figure analyses indicated that the PCMO films were grown epitaxially with a (001) normal orientation on the YBCO/LAO structure with an especially high degree of in-plane atomic ordering referenced by a 0.4° full width at half maximum (FWHM) of the PCMO (024) peak in the x-ray ϕ scan.

Silver contact pads of radius $r \approx 0.4$ mm and a nominal separation of 5 mm were sputtered on top of the PCMO and on the YBCO layers in PCMO/YBCO bilayer samples. Electrical pulses of 100 ns duration were applied across the PCMO film through these contacts. The resistance between the two electrodes was measured after each pulse. At room temperature, and under zero applied magnetic field, the measured resistance of the PCMO film was observed to change after the peak voltage of the applied pulse was increased above a threshold value (approximately 5 V). It was found that the resistance of the PCMO film could either be decreased or increased according to the pulse polarity. The resistance change also depended on the pulse magnitude, the pulse number, and the sample resistance change history.

The resistance versus pulse number for a PCMO/YBCO bilayer sample is shown in Fig. 1. The sample resistance decreases precipitously when positive pulse goes from PCMO layer to YBCO layer, reaching a saturation low value under accumulating pulses of the same polarity and peak voltage. Upon reversing the direction of the pulsed field, the resistance increases to a high saturation value with increasing number of pulses. Subsequent changes of the pulsed field direction reverse the resistance change of the PCMO film resulting in an electrically reversible variable resistance for the PCMO. Such behavior has been reproduced for more than 30 separate samples. It should be noted that a given resistance state was stable with time at room temperature, exhibiting a resistance variation of less than 1.5% over 2×10^5 s.

The extent to which a sample is affected by electrical pulses can be defined as the EPIR ratio: $\Delta R/R_{\text{MIN}} = (R_{\text{MAX}} - R_{\text{MIN}})/R_{\text{MIN}}$, where R_{MAX} and R_{MIN} are the maximum and minimum nonvolatile resistances induced by electrical

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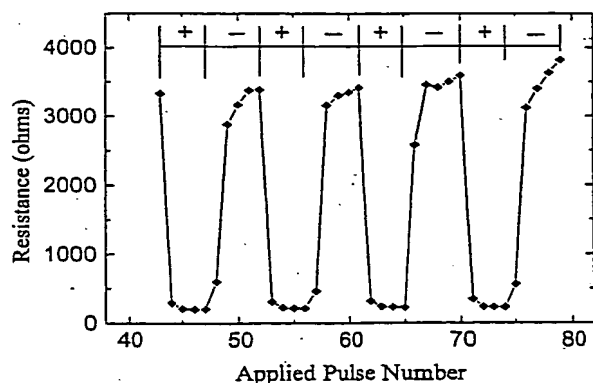


FIG. 1. Nonvolatile resistance vs electrical pulse number for a $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin film sample measured in zero applied magnetic field and at room temperature (23°C) under 18 V height and 100 ns length pulses. The + and - indicate change in applied pulse polarity.

pulses. Figure 1 shows that a room temperature EPIR ratio as large as 1770% has been obtained in PCMO. The EPIR ratio has been shown to depend, among other things, on the crystalline and compositional quality of the PCMO film. It is therefore expected that a larger EPIR ratio will be achieved as sample processing is improved.

Single layer PCMO samples (PCMO grown on LAO) were also studied to help identify whether the observed resistance change phenomenon is an interface-driven effect or an intrinsic one in CMR materials. Four Ag contact pads were deposited on top of a PCMO film, and resistivity was measured by the standard dc four-probe technique. Reversible nonvolatile resistance changes were reproduced in the single layer sample, with however, a lower overall EPIR ratio than the bilayer samples. This is principally due to the comparatively large distance between the two inner electrodes, which leads to a lower overall electric field in the film, and therefore a lower EPIR ratio. The measurable EPIR effect in the single PCMO layer sample at room temperature indicates that the effect is likely intrinsic to CMR materials. This is further supported by preliminary results from LaCaMnO_3 thin films, which also show EPIR behavior.

Figure 2 shows a lifetime test for a PCMO/Pt sample to which nearly 12 000 pulses of 51 V height and 108 ns width were applied at 10 Hz frequency. The pulses were applied such that seven negative pulses were followed by three posi-

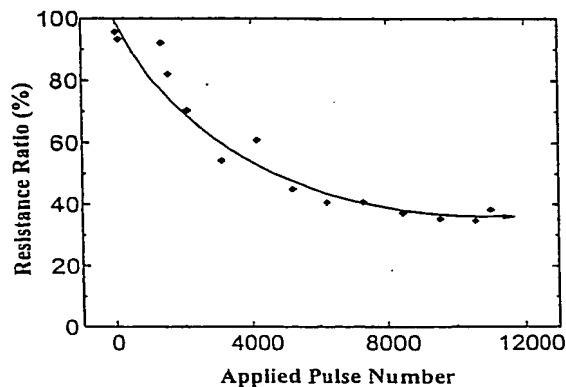


FIG. 2. The normalized nonvolatile resistance ratio vs pulse number for a $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{Pt}$ thin film sample measured for large numbers of pulses at room temperature and in zero applied magnetic field.

tive ones, effectively switching the PCMO layer from high to low resistivity states. It can be seen from Fig. 2 that the EPIR ratio gradually decreases with increasing pulse number, but that it reaches an approximate saturation nonzero value at high pulse number ($>5 \times 10^3$). Similar results were obtained for PCMO/YBCO/LAO samples. It is important to note here that the reversible resistance change effect is observed for the PCMO samples grown both on YBCO and on Pt bottom electrodes, thereby separating the EPIR effect from the type of substrate used (oxide or metal).

The EPIR effect occurs in the paramagnetic insulating state of the $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, and is nonvolatile and reversible. Several examples exist of external stimuli, other than magnetic field, transforming the PCMO insulating state to a metallic magnetically ordered ferromagnetic state. These examples, which include optical stimulation¹¹ and electric field stimulation,⁸ all are volatile and nonreversible, and most of them are effective only at low temperatures (below T_c).

In some of the above cases, nucleation of metallic filamentary paths was proposed, however, only at low temperatures and with volatility of state. We also believe that filamentary high conductivity paths are responsible for the electric-pulse-induced resistance change effect reported here, however, the paths are nonvolatile with respect to removal of the pulsed electric field, and occur in the insulating paramagnetic state. As a result, other mechanisms are sought as the basis for this effect. Ferromagnetic clusters associated with magnetic polarons, which can exist above T_c ¹² have been referenced as a possible basis for the standard low temperature CMR effect. Within the present work, the applied strong electrical field (under pulsing) could change the shape of such ferromagnetic clusters, and arrange them directionally from an expected random state to an organized state. An improved percolation path for charge carriers through the conductive clusters could be realized resulting in filamentary paths of increased conductivity. Reversing the pulsed field could reshape the polarized clusters and rearrange them into a secondary organized state. Because of the collective behavior of the charged clusters, the rearrangement of the polarized clusters from one organized state to a secondary organized state may result in a secondary state with higher resistance. This is consistent with observations that if at first a positive pulse is used to decrease sample resistance, then reversing the pulse polarity only increases the resistance.

Further, electric fields can, combining with the anisotropy along the film normal, cause field-direction-dependent lattice distortions. It has been reported that specific combinations of stretching and compression of the Mn-O bonds in $\text{Re}_{1-x}\text{Ca}_x\text{MnO}_3$ materials can favor localization or delocalization of charge carriers through electron-lattice coupling¹³ thus changing the insulating state of the paramagnetic PCMO.

The presented EPIR effect is a unique response of a material to external stimulation. The value of the resistance of a sample can now be electrically varied at will over a large range, thus presenting a variety of possible applications including electrically variable thin-film resistors and resistive high-density nonvolatile memory elements. Work currently underway will further develop these and other aspects of the electric-pulse-induced reversible resistance change effect,

leading to both new applications and a more complete description of the basis for the effect.

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